

## CLAIMS

1. A method for operating a quadrupole ion trap in mass spectrometry, the method comprising:
  - determining a calibrated resonant frequency for precursor ions in a first ion population in an ion trap;
  - determining a frequency adjustment for the precursor ions in a second ion population based on the number of ions in the second ion population; and
  - operating the ion trap using an adjusted resonant frequency that is based on the calibrated resonant frequency and the determined frequency adjustment.
2. The method of claim 1, wherein:
  - operating the ion trap using the adjusted resonant frequency includes operating the ion trap including the second ion population.
3. The method of claim 1, wherein the number of ions in the second ion population is substantially larger than the number of ions in the first ion population.
4. The method of claim 3, wherein the number of ions is sufficient to result in substantial space charge effects in the second ion population.
5. The method of claim 1, wherein:
  - operating the ion trap based on the adjusted resonant frequency includes exciting the precursor ions in the ion trap at the adjusted resonant frequency.
6. The method of claim 5, wherein:
  - exciting the precursor ions at the adjusted resonant frequency includes fragmenting the precursor ions in the ion trap to generate product ions.
7. The method of claim 6, the method further comprising:
  - ejecting one or more product ions from the ion trap based on the mass-to-charge ratios of the product ions.
8. The method of claim 7, further comprising:
  - analyzing the mass-to-charge ratios of the ejected product ions.

9. The method of claim 8, wherein:  
analyzing the mass-to-charge ratios of the ejected product ions includes analyzing the mass-to-charge ratios of the ejected product ions in an FTICR mass analyzer.
10. The method of claim 1, further comprising:  
trapping the precursor ions in the ion trap with an oscillating multipole potential having an amplitude; and  
adjusting the amplitude of the oscillating multipole potential to set the adjusted resonant frequency.
11. The method of claim 1, wherein:  
the adjusted resonant frequency is smaller than the calibrated resonant frequency.
12. The method of claim 1, wherein:  
determining the frequency adjustment for the precursor ions in the second ion population includes estimating the number of ions in the second population.
13. A method for determining a resonant frequency for a population of ions in an ion trap, the method comprising:  
receiving a calibrated resonant frequency for precursor ions in a first ion population in an ion trap;  
receiving an estimated number of the ions in a second ion population in the ion trap; and  
using the estimated number of the ions and the calibrated resonant frequency to determine an adjusted resonant frequency for the precursor ions in the second ion population.
14. The method of claim 13, wherein using the estimated number of the ions to determine the adjusted resonant frequency includes:  
determining a frequency adjustment based on the estimated number of the ions;  
and  
adjusting the calibrated resonant frequency using the determined frequency adjustment.

15. The method of claim 13, wherein the number of ions in the second ion population is sufficient to cause substantial space charge effects in the second ion population in the ion trap.

16. A software product, tangibly embodied in a machine-readable medium, for determining a resonant frequency for a population of ions in an ion trap, the software product comprising instructions operable to cause one or more data processing apparatus to perform operations comprising:

- receiving a calibrated resonant frequency for precursor ions in a first ion population in an ion trap;

- receiving an estimated number of the ions in a second ion population in the ion trap; and

- using the estimated number of the ions and the calibrated resonant frequency to determine an adjusted resonant frequency for the precursor ions in the second ion population.

17. The software product of claim 16, wherein using the estimated number of the ions to determine the adjusted resonant frequency includes:

- determining a frequency adjustment based on the estimated number of the ions;
- and

- adjusting the calibrated resonant frequency using the determined frequency adjustment.

18. The software product of claim 16, wherein the number of ions in the second ion population is sufficient to cause substantial space charge effects in the second ion population in the ion trap.

19. A mass spectrometry system, comprising:

- means for determining a calibrated resonant frequency for precursor ions in a first ion population in an ion trap;

- means for determining a frequency adjustment for the precursor ions in a second ion population based on the number of ions in the second ion population; and

- means for operating the ion trap including the second ion population using an

adjusted resonant frequency that is based on the calibrated resonant frequency and the determined frequency adjustment.

20. The system of claim 19, wherein the number of ions is sufficient to result in substantial space charge effects in the second ion population.

21. The system of claim 19, wherein:  
the means for operating the ion trap is operable to excite the precursor ions in the ion trap at the adjusted resonant frequency.

22. The system of claim 21, wherein:  
the means for operating the ion trap is operable to fragment the precursor ions in the ion trap based on the adjusted resonant frequency to generate product ions.

23. The system of claim 22, wherein:  
the means for operating the ion trap is operable to eject one or more product ions from the ion trap based on the mass-to-charge ratios of the product ions.

24. The system of claim 23, further comprising:  
a mass analyzer to analyze the mass-to-charge ratios of the ejected product ions.

25. The system of claim 24, wherein the mass analyzer is an FTICR mass analyzer.

26. A mass spectrometry system, comprising:  
a source of ions;  
an ion trap operable to receive ions from the source of ions; and  
a controller to control the ion trap, the controller configured to perform operations including:  
determining a calibrated resonant frequency for precursor ions in a first ion population in the ion trap;  
determining a frequency adjustment for the precursor ions in a second ion population based on the number of ions in the second ion population; and  
operating the ion trap using an adjusted frequency that is based on the calibrated resonant frequency and the determined frequency adjustment.

27. The system of claim 26, wherein:  
the controller is configured to fragment the precursor ions in the ion trap based on the adjusted resonant frequency to generate product ions.
28. The system of claim 27, wherein:  
the controller is configured to eject one or more product ions from the ion trap based on the mass-to-charge ratios of the product ions.
29. The system of claim 28, further comprising:  
a mass analyzer to analyze the mass-to-charge ratios of the ejected product ions.
30. The system of claim 29, wherein the mass analyzer is an FTICR mass analyzer.